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Developments in water quality monitoring and management in large river catchments using the Danube River as an example

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Abstract

Effective management of water quality in large rivers requires information on the influence of activities within the catchment (urban and rural) throughout the whole river basin. However, traditional water quality monitoring programmes undertaken by individual agencies normally relate to specific objectives, such as meeting quality criteria for wastewater discharges, and fail to provide information on basin-scale impacts, especially in transboundary river basins. Ideally, monitoring in large international river basins should be harmonised to provide a basin-scale assessment of sources and impacts of human activities, and the effectiveness of management actions. This paper examines current water quality issues in the Danube River basin and evaluates the approach to water quality monitoring in the context of providing information for a basin-wide management plan. Lessons learned from the monitoring programme in the Danube are used to suggest alternative approaches that

could result in more efficient generation of water quality data and provide new insights into causes and impacts of variations in water quality in other large international river basins.

Keywords: Danube River basin, water quality monitoring, international river basins, transboundary rivers, monitoring networks

1. Introduction

River water quality globally has been impacted by anthropogenic activities, in many cases in ways that still have to be fully quantified (e.g. Meybeck, 2005; Vörösmarty, 2002). Whilst these impacts are increasingly acknowledged, our ability to understand the magnitude of anthropogenic forcing is constrained by the limited availability of long-term water quality data-sets, which are essential in understanding system behaviour (Burt et al., 2014; Myroshnychenko et al., 2015).

Large river basins pose many challenges with respect to water quality monitoring and management, particularly in multi-national basins where individual countries may differ in their legislative framework and in their priorities for water resource management (Bloesch et al., 2012; Sommerwerk et al., 2009). However, the main aim in all cases is ultimately the sustainable management of water resources (UNEP 2007). The focus in international river basin management has largely been on water quantity and flow allocation, particularly where there has been a high demand for energy from hydropower, water for irrigation, and/or problems related to flood control and the role of wetlands (Rebelo et al., 2013). The physical, chemical and biological quality of river water is critically important, because they are linked to every aspect of human wellbeing and sustainable development (UN 2012). Therefore, monitoring water quality is essential in determining the impacts of human activities, the suitability of water for human use and fluxes (through concentrations and discharge measurements) of sediment and contaminants to lakes and coastal zones. Such monitoring typically has a local focus, but to contribute to management at the river basin scale it is essential to harmonise individual monitoring activities to: i) indicate trends over time; ii) obtain a complete picture of the impacts of activities, and their interaction, within the basin; iii) determine downstream impacts; and iv) direct remedial actions most appropriately.

This paper considers current problems (and opportunities) of water quality monitoring specifically in the Danube River Basin (DRB) of Central and Eastern Europe. In common with many other catchments, the DRB has experienced significant recent changes in water quality, including physical, chemical and biological water quality. The challenges faced in the DRB are examined here, highlighting the importance of adopting a holistic approach when investigating water quality

problems. The situation in the DRB is compared and contrasted with other large river basins and ways in which monitoring of river water quality can be improved are identified.

2. The Danube River Basin: features and pressures

The DRB is Europe's second largest river basin, with a catchment area of 801,463 km² and a total channel length of 2,857 km. It is the world's most international river basin, including territory from 19 countries: 29% of the basin is within Romania, Hungary lies entirely within the Danube basin and large proportions of Austria, Serbia and Slovakia are in the DRB. Fourteen of the countries in the basin have co-operated on water protection and conservation since 1998 through the International Commission for the Protection of the Danube River (ICPDR), which is working to implement the 1994 Convention on Cooperation for the Protection and Sustainable Use of the Danube River, known as the Danube River Protection Convention (DRPC). This Convention has the objective of achieving sustainable and equitable water management, including the conservation, improvement and the rational use of surface and ground waters in the DRB. Of the 14 countries, nine (Austria, Bulgaria, Croatia, Czech Republic, Germany, Hungary, Slovakia, Slovenia and Romania) are members of the European Union (EU) and are bound by the Water Framework Directive (WFD), Directive 2000/60/EC, (EC 2000) which came into force in December 2000 (although the actual date of its implementation varies according to when countries joined the EU). Subsequent directives, 2008/105/EC on Environmental Quality Standards (EQS) in the field of water policy (EC 2008), as amended by daughter Directive 2013/39/EU (on priority substances), also have implications for catchment management; and all the countries co-operating under the DRPC have agreed to implement the WFD and the daughter Directives in the basin through the ICPDR.



Figure 1. Dams and weirs along the length of the Danube River, indicating those that block the natural migration patterns of migratory fish species (both diadromous and potamodromous) by preventing access to spawning grounds (Source: ICPDR)

One of the key characteristics of the Danube River today is the extent to which the flow of the Danube (and its principal tributaries) has been increasingly regulated for hydropower and navigation (see Habersack et al., 2016). This has considerable implications for water quality, including temperature (Webb and Nobilis, 2007) and sediment flux (Schwarz et al., 2008). At present there are 598 major dams and weirs along the Danube and its tributaries (ICPDR 2014), 156 of which are for hydropower (Sommerwerk et al., 2009). In the first 1100 km of the Danube, there is an average of one power plant every 16 km above the Gabčíkovo-Bös Water Barrage System (GB-WBS) in Slovakia/Hungary (ICPDR 2014). In Hungary the biggest abstraction of water from the Danube is at the Paks nuclear power plant ($Q = 100 \text{ m}^3 \text{ s}^{-1}$) which is responsible for thermal pollution in the river. In total, there are 69 dams along the main stem of the Danube and ~30% of the channel length is impounded, with implications for species migration (Figure 1) and sediment transport (Klaver et al., 2007). In addition to dam construction for hydropower, the channel and banks have been engineered to facilitate navigation and improve flood protection. Such changes have implications for aquatic habitats and the river ecology as well as the associated floodplain and wetland habitats (Habersack et al., 2016; Hein et al., 2004; Hohensinner et al., 2005; Rebelo et al., 2013). Compared with the 19th Century, estimates

suggest 65% to 81% of the former floodplain area has been lost (ICPDR 2009; Schneider 2002), with large differences between the different river sections (i.e. upper, middle, lower and delta).

In addition to the direct effects of anthropogenic activities in the DRB, there are significant impacts associated with other long-term processes such as climate change, similar to those discussed for the neighbouring upper Rhone Basin by Clarvis et al. (2014). The ICPDR Strategy for Adaptation to Climate Change (ICPDR 2013a) predicts an increase in mean winter discharge and a decrease in mean summer discharge for the entire DRB, although there will be seasonally local variations as predicted for the Mures River (Sandu et al., 2009). The predicted increase, especially in winter floods and run-off, may increase particle transport and particle-associated water pollution, depending on the contaminants stored in the sediments and the grain sizes of the bed sediments (Pulley et al., 2016; Vignati et al., 2003). Water temperatures are also expected to increase with associated decreases in water quality (e.g. reduced oxygen concentrations and increased algal blooms). The precise impacts of climate-associated problems in the DRB are hard to quantify, but the GB WBS hydropower plant illustrates some of the anticipated effects on surface waters in the basin. Construction of the GB WBS in 1992 led to the diversion of the main channel of the Danube and resulted in a reduction of discharge from 2000 to 400 m³s⁻¹ as the majority of the river flow was diverted for input to the hydropower plant (Kovács et al., 2015). In consequence, shallow groundwater levels in the immediate vicinity have fallen significantly (Bárdossy and Molnár, 2003; 2004), to levels that are comparable to recent IPCC projections (IPCC 2013). Given the decreased discharge, more sediment is now deposited on the river bed leading to river bed clogging (colmation) and decreased groundwater recharge (via effluent seepage), resulting in conditions that would have normally occurred only in dry years and which are now anticipated under future climate change predictions to occur more frequently during summer in future (ICPDR 2013a).

3. Trends in water quality in the Danube River Basin

In common with many catchments, the DRB has experienced significant changes in water quality including: physical (e.g. temperature, suspended sediment and bed-load transport), chemical (e.g. ammonium, nitrate, nitrite, phosphorus and emerging pollutants) and biological water quality (faecal pollution, species loss and biological community alterations due to invasive species). These reflect multiple factors including changes in: i) land use; ii) point and diffuse pollution (from agriculture, industry and individual households), and iii) the catchment water cycle as a result of climate change and anthropogenic modifications of the drainage basin (see Sommerwerk et al., 2009 for a detailed overview of the DRB). One of the major water quality issues in parts of the DRB is organic pollution from untreated, or poorly treated, urban wastewaters. The impact of wastewater discharges has been clearly shown by marked increases in microbial faecal pollution downstream of major towns and cities, including Novi Sad, Belgrade, Budapest, Dunaföldvár, Zimnicea and Arges (Liska et al., 2015).

Quantifying pollutants from diffuse sources is very difficult in large river basins; therefore point and diffuse nutrient emissions into the Danube have been estimated using the MONERIS (MOdelling Nutrient Emissions in RIver Systems) model (Behrendt et al., 2007). The results indicated that agriculture was the major source of N emissions but that this was not as significant as urban settlements for P emissions (ICPDR 2009). Improvements are planned or underway for most urban wastewater treatment plants in the DRB including new and additional treatment technologies and adapted capacities, especially those serving large agglomerations such as Bucharest, and also in other EU member countries (see Annex 2 of ICPDR 2012). Similarly, the numerous identified industrial sources throughout the EU member countries in the DRB, are gradually being addressed by the Integrated Pollution Prevention and Control (IPPC) Directive (EU 2010) and related legislation (ICPDR 2012). Improvements in water quality, in terms of ecological and chemical status, should be evident once all such measures are fully implemented over the next decade.

At present, the effects of eutrophication are evident throughout the catchment (Oguz et al., 2008a). However, the situation varies through the DRB: typically in the upper basin, river reaches are characterized by good water quality (albeit with a highly regulated flow regime), whilst water quality is poorer in the lower basin, especially in specific tributaries of the Danube (see reports of JDS 1, JDS 2 and JDS 3: Literáthy et al., 2002 and Liska et al., 2008, 2015 respectively). In the 1970s and 1980s, the Danube was estimated to contribute 80% of the riverine nutrient load to the Black Sea (Oguz et al., 2008b). Dissolved inorganic nitrogen (DIN) and phosphate concentrations in the Black Sea increased from 1 to 8 μM and from <2 to 3–8 μM respectively (Oguz and Velikova, 2010). Over the same time period SiO_4 concentrations declined significantly (60 μM in 1970–1975 to 15 μM in 1980–1985) following construction of the Iron Gates Reservoirs 1 and 2 (Humborg, et al., 1997; Teodoru and Wehrli, 2005). As a consequence of the increased N and P and the decline in Si (increase in N:P and N:Si ratios), there have been changes in the productivity and structure of the phytoplankton community in the Black Sea. In the 1970s, phytoplankton biomass increased by an order of magnitude and continued to increase until the early 1990s. Due to a decline in Si inputs, the phytoplankton community shifted from diatom-dominated (siliceous) to dinoflagellate-dominated (non-siliceous) (Oguz and Vilakova, 2010). Subsequently (2000–2005), the proportion of nutrient inputs to the Black Sea from the Danube declined to ~50% of the riverine nutrient load and there was a reduction of ~50% of the biochemical oxygen demand (BOD). Despite this, concentrations of inorganic nutrients remain 1.5 times higher than they were prior to 1950 (Oguz et al., 2008a). The decline in nutrient inputs probably reflects a combination of factors, including improvements in wastewater treatment (daNUbs Project Final Report 2005), nutrient retention (particularly P) in reservoirs (daNUbs Project Final Report 2005), the economic recession that occurred in many countries of the former Eastern Bloc, and reduced agricultural fertilizer use (Mee et al., 2005).

Results from JDS 3 show that metal concentrations in the sediments are at similar levels to previous surveys but there may have been a slight improvement compared with JDS 1 and 2, and target values were only exceeded at a few sites (Liska et al., 2015). Studies of trace elements in sediments of the Danube delta have shown that the main sources were from upstream, although overall the Delta sediments were less contaminated than the sediments in river reaches upstream in the catchment (Vignati et al., 2013; Woitke et al., 2003). There have also been marked changes in sediment transport as a result of interruptions to the continuum of bed-load transport with sediment deposition in impounded reaches and a sediment deficit in free-flowing river sections (Habersack et al., 2016). Sediment transport has been further modified by dredging for navigation, and by river engineering work, such as groynes, that contribute to increased river bed erosion in some reaches and sediment aggradation between groynes (Schwarz et al., 2008). River modifications can also interrupt the transport of sediments between the river and the floodplains. Maintaining river continuity (from the catchment headwaters downstream), and lateral connectivity between rivers and their floodplains, is important since both have wide-ranging environmental implications. For example, the effects of reduced sediment dynamics in impounded sections leads to wider ecological and environmental degradation including the clogging of hyporheic interstices. This results in reduced oxygen availability, the loss of fish spawning grounds and riparian zone degradation affecting benthic invertebrates and fish (e.g. Petkovska and Urbanič, 2015).

In common with many river basins, there is a lack of detailed knowledge of the levels of hazardous substances in the DRB, particularly persistent organic compounds, endocrine disruptors and pharmaceutical compounds (ICPDR, 2014). There is therefore an urgent need for chemical and effect-based monitoring tools to inform new models of exposure and risk assessment (Brack et al., 2015). These require the application of sound science and, specifically, good understanding of pollutant sources, transport pathways and ultimately the fate of pollutants. Nevertheless, the sources of such contamination should be identified and controlled as a matter of priority in the DRB.

Fundamentally, catchment managers require significant help in identifying and monitoring specific compounds and appropriate ways of controlling or mitigating problems (such as untreated urban runoff). Addressing current water quality challenges requires a basin-scale approach providing a holistic view of the impacts of activities and their interactions within the basin, and new tools that build upon existing data-sets to model changes in key water quality determinants and improve the scientific basis for integrated catchment management. Examples of current needs are monitoring networks to capture spatial and temporal variability; standardisation of monitoring protocols; and combining real-time and basin-wide observational data. Within the DRB significant progress has already been made in the standardisation of monitoring protocols as outlined below.

4 Development of water quality monitoring in the Danube River Basin

Water quality throughout the DRB was first mapped by Liepolt (1967) and Schmid (2002; 2004) assessed water quality in the Danube basin in 1995 and 2002 based on benthic flora and fauna. Prior to 1998 when the ICPDR was formed, there was little basin-wide coordination of river monitoring but in December 1985 the governments of riparian countries along the Danube signed the Bucharest Declaration. One of its objectives was to improve the water quality of the Danube and, in order to comply with this objective, a monitoring programme of 11 cross-sections of the Danube River was established. The number of sampling sites was expanded to 61 stations in 1996 to form the Trans National Monitoring Network (TNMN). The TNMN aimed to provide sufficient data to enable reliable and consistent trend analysis for concentrations and loads of priority pollutants, to support the assessment of water quality for water use and to identify major pollution sources. Since the 1990s international co-operation in the basin has increased (ICPDR 2009). River water quality has continued to be a major focus of this co-operation, together with improvement of riverine ecosystems and management of groundwater quality (ICPDR 2014). With respect to the latter, 11 transboundary groundwater bodies have been identified in the DRB and at present it is estimated that ~72% of drinking water within the basin is derived from groundwater abstraction (ICPDR 2014).

The WFD required a revision of the TNMN and this was completed in 2007. The major objective of the revised TNMN is to provide an overview of the overall status and long-term changes of surface water and, where necessary, groundwater status in a basin-wide context with an emphasis on transboundary pollution. In response to the link between the nutrient loads of the Danube and eutrophication of the Black Sea noted above, sources and pathways of nutrients in the DRBD and the effect of measures taken to reduce the nutrient loads to the Black Sea have been a particular focus of monitoring effort.

To meet the requirements of the WFD and the DRPC the TNMN for surface waters currently includes:

- Surveillance monitoring I: Monitoring of surface water status;
- Surveillance monitoring II: Monitoring of specific pressures;
- Operational monitoring;
- Investigative monitoring.

Surveillance monitoring I and Operational monitoring entail the collection of aggregated data on surface water and groundwater status in the DRB and Surveillance monitoring II is a joint monitoring activity of all ICPDR contracting parties that produces annual data on concentrations and loads of chemical substances throughout the basin. Investigative monitoring is primarily a national task, but at a basin-wide level the Joint Danube Survey (JDS) was developed to carry out investigative

monitoring as required, e.g. to harmonize existing monitoring methodologies, to fill information gaps in the DRB monitoring networks resulting from an earlier focus on specific issues such as wastewater outfalls, and to test new methods or check the impact of “new” chemical substances in different matrices.

Surveillance monitoring I and Operational monitoring data are published in the DRB Management Plan. The ICPDR identified significant impacts and water management issues that should be addressed at the local and basin-wide scales and produced the first DRBD Management Plan in 2009. This, together with a programme of measures to improve water quality until 2015, is known as the Joint Programme of Measures (JPM) (ICPDR 2005; 2008; 2009). Implementation of the JPM was evaluated in 2012 (ICPDR 2012) and the second DRBD Management Plan is currently due to be completed by the end of 2015 (ICPDR 2013b).

Joint Danube Survey 3 - Overview map



Figure 2. The Danube River Basin showing monitoring sites for the Joint Danube Survey No. 3 in 2013 (Source: ICPDR)

Joint Danube Surveys have been undertaken at six year intervals since the first survey in 2001. The JDS 1 provided data for the entire river course for the first time covering > 140 biological, chemical and bacteriological parameters (Literáthy et al., 2002). These data were used in the first analysis of the DRBD according to WFD Article 5 (ICPDR, 2005). In 2007, JDS 2 produced a comprehensive

database of the status of the Danube and its major tributaries (Liska et al., 2008). The collected data complemented those from the TNMN surveillance monitoring focussing on a wide range of chemical parameters and providing reference data for biological quality elements. JDS 2 included the first systematic survey of hydromorphological parameters in the entire navigable channel of the Danube using a common method based on EN 14614 (CEN 2004). The results of the hydromorphological survey were available to the ICPDR Contracting Parties as a reference for developing the national methodologies and were also presented in the first DRB Management Plan in 2009. JDS 2 confirmed a generally improving trend for water quality along the Danube River and highlighted a number of specific problems, such as pollution by WFD priority substances and by newly emerging contaminants. JDS 2 also proved invaluable in improving the water quality assessment database and confirmed the need to undertake regular investigative monitoring exercises. The report from JDS 3, which took place in 2013 (Figure 2), has been published recently (Liska et al., 2015). When planning JDS 3 major attention was given to addressing information gaps, such as sources of microbiological pollution and levels of priority pollutants, and the monitoring variables were set accordingly. The WFD allows standards to be set for matrices other than water provided such standards guarantee the same level of protection as the water-based standards. Therefore, the analysis of priority substances in sediments, biota and suspended particulate matter are key objectives of the Joint Danube Surveys. JDS 3 reconfirmed that the Danube flora and fauna show a high degree of biodiversity. However, the results for WFD biological quality elements (e.g. fish, macrozoobenthos or macrophytes) demonstrate the need for further development and harmonization of methodologies applicable for the whole Danube River to evaluate the biological quality parameters necessary to determine the ecological status of the river according to the WFD. During JDS 3 several new analytical techniques and strategies were applied targeting hundreds of organic substances and resulting in the most comprehensive information in this area acquired to-date for the Danube. The analysis of these data enabled prioritization of the DRB specific pollutants. All the results and findings of JDS 3 provide a valuable resource for the Danube countries and are used for river basin management planning at both international and national levels, given the volume, character and homogeneity of the data. The generation of homogeneous data, which can be used for management purposes, is a key motivation for carrying out the surveys.

5. Lessons for future monitoring in the Danube

National water quality monitoring programmes across the DRB vary with respect to their spatial and temporal resolution. Moreover, the biological and chemical assessment protocols vary in different countries. Nevertheless, observations of Total Nitrogen and Total Phosphorus from JDS 3 showed high comparability with the time-corresponding data (August – September) from the long-term ICPDR surveillance monitoring (TNMN results from 2001 – 2011) (Liska et al., 2015). This confirmed the success of the on-going harmonisation process and improvement of operational activity

of the Danube National TNMN Laboratories network as well as the effectiveness of the Analytical Quality Control (AQC) programme organised by the ICPDR at the basin level. The WFD requires reference conditions to be defined for all water bodies for both abiotic and biotic characteristics, and appropriate monitoring must be undertaken (Pardo et al., 2012). However, determining reference conditions requires considerable understanding of hydromorphological and biological conditions, as well as their interaction (Reyjol et al., 2014). Meeting these criteria has been a major task throughout EU countries, and harmonisation of approaches is particularly challenging in multi-national river basins, such as the DRB. Ensuring comparability of national assessments across Europe requires an inter-calibration exercise, as required by the WFD, but this is still an ongoing issue in large river basins >10.000 km² in area (Poikane et al., 2014).

5.1 Biological monitoring

The lessons learned from JDS 3 will help ensure proper planning and design of future ICPDR monitoring activities. Future surveys will select sites for hydromorphological assessment in close cooperation with monitoring and biological experts, to ensure the use of representative river sections. Hydromorphological assessments, particularly for large rivers, should be based on physical processes, such as discharge and flow patterns. The link between hydromorphological parameters and biological responses, together with the related monitoring efficiency, also needs to be improved. The first steps in this direction have already been taken by performing in-situ measurements during JDS 3 of discharge, velocity (flow pattern, surface velocity), cross sections, bed material, suspended load, water level fluctuation, and water level slope. Future monitoring will take fully into account the type-specific conditions according to WFD requirements. Moreover, the sampling methods applied for the benthic macroinvertebrates were found to complement each other: the multi-habitat sampling method is especially applicable for ecological status assessment of large rivers at low water periods due to its standardized, stressor-specific and habitat-oriented approach (Liska et al, 2015). Kick and sweep methods can provide additional information particularly on mussel populations inhabiting deeper zones next to the bank. Deep water sampling is not affected by water level and discharge and is, therefore, appropriate for data collection throughout the river basin.

The JDS 3 results also confirmed that despite the methodological limitations related to phytobenthos in large rivers, diatoms are valuable indicators of water quality and of the general degradation of the Danube, and can be reliably applied to the assessment of the ecological status of the river (Liska et al., 2015). Moreover, the results of the JDS 3 macrophyte study demonstrated that a macrophyte-based quality assessment of large rivers is possible. It has been suggested that biological assessment systems deliver plausible results only for the river-types or regions for which they were developed. In this context the findings of dissimilarities and similarities between river-sections supports the necessary region- and river-type-specific adaptations of ecological quality assessment. A further outcome of the

macrophyte study was the importance of including helophytes and selected bank-vegetation in a macrophyte-based quality assessment, especially with respect to hydromorphology. The national fish indices applied during JDS 3 (FIA, FIS, EFI – Liska et al., 2015) delivered inconsistent results for the whole river course indicating that they react to different stresses (hydromorphology vs. water quality) and are only applicable for restricted river stretches. Hence additional sampling methods (e.g. trammel nets) would be required to complete the data set, particularly benthic fish species in the Lower Danube (Szalóky et al., 2014).

5.2 Faecal indicators and emerging pollutants

For the purpose of managing human inputs to surface waters from point and diffuse sources, microbiological monitoring has often been neglected despite its importance for human health and its potential to locate sources and even to identify whether the source is of human or animal origin (Hagedorn et al., 2011). In Europe, large spatially distributed datasets of faecal indicator organism (FIO) flux within catchments are scarce because FIOs and pathogens are not listed as a regulatory parameter of river quality (Kittinger et al., 2013; Reder et al., 2015). As a result, there is limited evidence of good practice and lessons learned for the design of sampling regimes for complex transnational river basins. However, using experience gained in JDS 2, microbiological monitoring in JDS 3 was expanded to include source tracking and to sample at three stations across the width of the river at each sampling location (Liska et al., 2015) because significant differences in FIOs at opposite sides of a river have been shown in other studies (Quilliam et al., 2011). Unfortunately, implementing the JDS in the summer months only, with constant low flow conditions, could lead to a systematic bias to base-flow conditions (Kay et al., 2005; McKergow and Davies-Colley, 2010). Evidence suggests that there is at least an order of magnitude difference in FIO concentrations observed during base versus storm flow events (Kay et al., 2005; Tornevi et al., 2014). Tetzlaff et al. (2012) have suggested that seasonal-based studies have led to an imbalance in understanding winter versus summer contributions to year-round microbial pollution of receiving waters and results from summer sampling only should be interpreted accordingly for management purposes. In order to address policy-orientated questions concerning impacts of agricultural intensification or climate change on microbial water quality, a nested sampling design within large catchment systems is required to facilitate understanding and appreciation of scaling implications of microbial water quality signals through the catchment continuum (e.g. Harclerode et al., 2013; Meays et al., 2006; Tetzlaff et al., 2012; Traister and Anisfeld, 2006).

The parameters included in any monitoring programme depend on the objectives of the programme and for large river basin monitoring programmes with multiple objectives, such as the JDS, the number and range of parameters can be extensive. For example, more than 800 parameters were analysed in JDS 3 in 2013, including chemical, microbiological, ecotoxicological, radiological, and

biological, at a cost of approximately €2 million (Liska et al., 2015). With such a large investment, major benefits for water quality through improved understanding and management will be expected, as well as more targeted selection of parameters for future monitoring. During JDS 3, samples were screened for 650 targeted organic pollutants and several hundred more were tentatively identified for future evaluation. This non-target screening was found to be useful in identifying specific river basin pollutants, but a strategy is needed to reduce the amount of detected substances in a single sample to 'workable' numbers (a maximum of 10 – 100 substances). Selecting the appropriate compounds is a topic of current concern for all water quality programmes, including at the European level in the WFD (Carere et al., 2012). One possibility would be to prioritise non-target screening data, which is being considered by the NORMAN Working Group on Prioritisation (www.norman-network.net). Other approaches based on risk assessment and modelling emissions from dispensing data, could also prove useful in assisting in selection of the compounds likely to present the greatest environmental or human health risk in water bodies (Bottoni et al., 2010; Brack et al., 2015; Cooper et al., 2008; Daughton, 2014; Kugathas et al., 2012; Oosterhuis et al., 2013; Wajsman and Rudén, 2005;). JDS 3 also demonstrated the feasibility of effect-based screening at a river basin-wide scale using on-site, large volume extraction even under conditions of high dilution. Similarly, a combination of passive samplers with bioassays appeared to be very promising in detecting trace organic pollutants and toxic potentials along the river and identifying areas of concern for further investigation (Liska et al., 2015).

5.3 Options for site selection

Water bodies should be monitored at a spatial scale that provides information on their current state and highlights where new management actions may be needed, or if current management practices are sufficient (Reyol et al., 2014). Hence, the greater the number of monitoring sites throughout the water body, the higher the probability that they will accurately represent its current state. However, there are resource implications where a large number of monitoring sites are required and a balance is needed between resource requirements and scientific rigor (Earle and Blacklocke, 2008).

In order to generate the data required to enable efficient water quality management across the DRB, it is necessary to harmonize sampling approaches and periodically re-adjust the monitoring network (i.e. the spatial and temporal scales of monitoring and the techniques adopted). This can only be achieved by drawing upon data sets from existing monitoring networks, including national survey programmes and the JDS. These can enable periodic and systematic recalibration to ensure the monitoring data are as fully representative of the basin as possible.

Computational methodologies which specifically focus on estimating sampling frequency (temporally and spatially) can help optimize monitoring design, avoiding significant loss of information. For example, in riverine monitoring, it is generally accepted that sampling sites should be situated at the

mouth of principal tributaries (Sharp, 1971). However, river reaches between tributary confluences can be subject to numerous influences, including structures for hydropower generation (Kovács et al., 2015), and urban (Booth et al., 2004; Konrad and Booth, 2005), industrial (Vignati et al., 2013) and agricultural effluent (Lenat, 1984). Therefore, increasing the number of monitoring sites in “uncovered” sections of the basin would be logical. However, the current tendency is to reduce the number of monitoring sites wherever possible, to reduce costs. Throughout river basins most monitoring authorities seek to find groups of sampling sites which can be replaced with a single representative monitoring station. In any event, the principle is that if two or more sites show the same trend with respect to similar influences, then the additional sites can be considered redundant and discarded. Monitoring sites can be grouped manually (based on professional experience, intuition etc.) or by using, for example, multivariate statistics. Grouping algorithms, such as cluster analysis (CA) are frequently used to find sampling sites that respond similarly. Dimension reduction methods, such as principal component -, factor-, or redundancy analysis, have also been used (for examples see Cansu et al., 2008; Neilson and Stevens, 1986; Simeonov et al., 2003; Singh et al., 2004; Zeng and Rasmussen, 2004;). Canonical correspondence analysis and artificial neural networks (Khader and McKee, 2014), such as self-organized maps (Khalil et al., 2011), have also been applied to explore the spatial or temporal structure of the data.

If sampling is infrequent or not equidistant in time, the site representativeness may be questionable (Buonaccorsi, 2010). The higher the variability (coefficient of variation in time), the more frequent sampling is needed to obtain the same accuracy, and *vice versa* (Clement, 2001). The most straightforward approach when considering/revising monitoring design is variography, which can estimate the boundaries of an acceptable sampling frequency in time and space separately, based on the fact that samples outside the temporal (Kovács et al., 2012) or spatial (Hatvani et al., 2014) range are essentially independent (Webster and Oliver, 2007).

In some cases, the problem of spatial grouping of sites, and/or temporal grouping of sampling events, has been solved using new techniques. For example, Yang et al. (2012) used a multi-label classification to manage flood retention basins, as did Straatsma et al. (2013) who assessed uncertainty in hydromorphological and ecological model outputs caused by errors in the land cover classification in the Rhine River floodplain. Nevertheless, the problem of handling both the temporal and the spatial variability remains. This can be addressed by combining CA with discriminant analysis (DA), providing a new method called Combined Cluster and Discriminant Analysis (CCDA), which accounts for the full variance, and identifies similar and homogeneous groups of sampling sites (Kovács et al., 2014). By coupling the temporal and spatial characteristics of a water-quality dataset, statistical analysis should help implement the WFD. The number of sampling sites required to represent a water body fully can be determined by CCDA, thus objectively optimizing the monitoring

network. The sites in each homogeneous group measure the same phenomena and are therefore redundant, and can be replaced by one site. While a reduction in the size of the network reduces costs, determining the exact saving is complicated as it is not equal to the percentage of the number of sites abandoned. When monitoring a water body, the basic infrastructure and personnel have to be available at all times, even if there is only one functioning sampling site. Nevertheless, if each sampling site is managed by a different authority, equipped with their own instrumentation and personnel, the ratio of sites abandoned will equal the ratio of money saved (for a direct example on the Danube and its tributary the Raab, along with an expanded discussion on the topic, see the Appendix or for further examples see Kovács et al. (2015) and Tanos et al. (2015).

The question still remains: of the sites clustered in one homogeneous group, which site should be retained, or which site abandoned? In the case of rivers, which are linear systems, this question can also be answered using CCDA, by attributing a factor (termed pairwise difference) to the neighboring sampling sites showing their difference (Figure A1a). Where these differences are the lowest, then the site can be abandoned, whereas if all sites have unique information (and do not form a homogeneous group) then all should be kept. However, by assessing their pairwise differences, and finding the highest, instances where an additional sampling site is required can be identified. In an optimal setting the resources released by discontinuing monitoring at redundant sites may be used to set up new sites thus producing a more representative monitoring network.

It is important, however, that the temporal resolution of the monitoring sites is also considered in any future recalibration of the JDS network. For example, if a decision is made to abandon one of two sites, then the one with longest records should be kept. These long-term sampling sites are those which will enable the impacts on water quality resulting from significant changes, such as installment of hydropower plants, waste water treatment plants etc., or the occurrence of invasive species, to be assessed.

6. Discussion

Fundamental to a successful water quality monitoring programme are carefully written objectives leading to the information needed for appropriate management action (Meybeck et al., 1996) and consecutively the integrated evaluation of the conclusions drawn from the observations (Knieper et al., 2010). The objectives should be sufficiently clear to define the location of sampling sites, the parameters to be measured, the associated quality assurance, frequency of measurement and the programme duration. Within the context of the Danube River, the TNMN has the primary objective of determining status and long-term trends in surface water quality and loads, whilst the JDS fills information gaps in the monitoring network and undertakes investigative monitoring with more

specific objectives. The level of co-operation in monitoring activities between riparian countries in the Danube basin exceeds that in many other major international river basins: for example, the JDS generates comparable data for the whole Danube River using harmonised methods. Another international river, the Mekong, flows through six countries: China, Myanmar, Thailand, Lao PDR, Cambodia and Vietnam. Data have been collected in the Mekong continuously since 1985 through its Water Quality Monitoring Network (WQMN), which is operated by designated national laboratories (MRC 2015). All laboratories follow agreed sampling and analysis protocols and adhere to the consistent quality assurance/quality control procedures yielding data that are temporally and spatially comparable within the whole river basin. The outputs of both the Danube and Mekong monitoring programmes are of sufficient quality to evaluate the state of the whole river and to inform planning and management at river basin level (ICPDR 2009; MRC 2010; MRC Environment Programme 2013). In contrast, integrated water resources management in the Amazon basin is hampered by the fact that each riparian country has several different agencies monitoring and managing water quality and there is no inter-calibration or standardisation between agencies (Nascimento and Fenzl, 2014). The Amazon basin is the world's largest drainage basin covering $\sim 6.1 \times 10^6 \text{ km}^2$ and seven countries: Brazil (69% of the basin), Bolivia, Peru, Colombia, Ecuador, Venezuela, and Guyana (de Souza et al., 2004).

A major concern in managing large river basins is the transfer of nutrients and pollutants from land-based activities to the deltas and coastal zones. This is a problem in the Danube basin: while there has been a reduction in nutrient loads from point sources (ICPDR, 2014; Sommerwerk, et al., 2009), diffuse sources still dominate N contributions at the basin-wide scale (ICPDR, 2014). The combination of historical patterns in eutrophication in the Black Sea over previous decades, the impacts of nutrient ratios on food web structure, and the continued elevated levels of nutrient inputs to the Black Sea from the Danube (as discussed in Section 3), highlight the importance of continued long-term monitoring in the whole river basin to optimize measures to be taken. This is a common problem in large river basins: the need to address basin level water quality issues has also been highlighted for the Mississippi River (Committee on Clean Water Act Implementation Across the Mississippi River Basin 2012; Perez and Walker 2014), where agricultural activities contribute between 70% and 80% of the N and P in the Gulf of Mexico (Alexander et al., 2008). Water quality monitoring activities in the Mississippi River are currently not particularly well co-ordinated at the river basin scale, and increased interstate co-operation is needed (Committee on the Mississippi River and the Clean Water Act, 2008).

As management of traditional pollution problems, such as nutrients, organic matter and heavy metals has improved, attention is turning to newly emerging contaminants such as endocrine disruptors and pharmaceutical compounds (Bottoni et al., 2010). There are 163 substances on the Candidate List of substances of very high concern under the REACH (Registration, Evaluation, Authorisation and

Restriction of Chemicals) Regulations (see ECEH 2015), whereas 33 priority substances and groups of substances have been listed in Annex II of the EU Directive on Environmental Quality Standards (2008/105/EC). The quality standards specified in this list were incorporated into the requirements of the Water Framework Directive (see EU 2015) and a further 12 substances were subsequently added in 2013 under Directive 2013/39/EU (EU 2013). The list includes pesticides and herbicides, some metals, and organic compounds such as polyaromatic hydrocarbons and polybrominated biphenylethers. In common with many other river basins, there is a lack of detailed knowledge of the occurrence and levels of hazardous substances in the waters of the Danube and its tributaries (ICPDR 2014) but JDS 3 incorporated monitoring of priority substances in water, particulate matter, sediments and biota and obtained the first comprehensive overview for the river basin (Liska et al., 2015). Monitoring of newly emerging pollutants requires good understanding of sources, transport pathways, and ultimately the fate of the pollutants (Hughes et al., 2012; ter Laak et al., 2010). It has been recognised for several decades that aquatic organisms can accumulate many toxic pollutants and magnify the level of accumulation through the food web. Determining pollutant concentrations in aquatic biota can, therefore, provide a useful monitoring approach in some situations (Philips, 1980; Samiullah 1990). This potential has now been embodied in the Environmental Quality Standards Directive 2008/105/EC (EC 2008) as a monitoring approach for use in relation to the WFD (Carere et al., 2012). Nevertheless, the number and types of new and emerging compounds present considerable challenges for catchment managers; for example in identifying and monitoring specific compounds and in identifying appropriate ways to control or mitigate specific problems (Brack et al., 2015; Cooper et al., 2008; Petrovic 2014).

Given the diversity of water quality problems that can occur in large rivers, it is essential that the relevant water quality parameters are monitored at appropriate spatial and temporal scales as well as being combined with new knowledge on significant pollution pathways affecting organisms (e.g. via food uptake). It is also important that monitoring programmes are evaluated periodically to ensure that the parameters being monitored and the monitoring sites are appropriate to meet the evolving objectives of the programme. Comparisons between data obtained from JDS 2 and JDS 3 have highlighted the need for sampling at stations across the width of the river for certain parameters, such as FIOs (Liska et al., 2015). Incorporating the emerging science of microbial source tracking into catchment studies to complement on-going monitoring and modelling activities can help in the identification of faecal pollution sources but it remains a largely qualitative approach. The availability of new molecular and enumeration techniques for FIOs is leading to increased interest in their potential for regulatory monitoring although there remains much debate in terms of practicality and cost associated with deployment (Oliver et al., 2010; 2014). With the increasing complexity of analytical methods that can, and may need to, be used in monitoring water quality in future in order to achieve effective management, alternative approaches to refining the scale (as described in section

5.3) and complexity of monitoring programmes are becoming more important. The role of modelling for predicting environmental concentrations, combined with risk assessment for the selection of priority pollutants are currently showing promise for smaller water basins (Kugathas et al., 2012) and the next challenge is to apply these techniques to larger international water basins such as the Danube.

7. Conclusions

Water quality monitoring in large, multi-national river basins presents particular challenges for harmonising the approaches used across the different agencies and government bodies responsible for monitoring and managing water quality, at the same time as fulfilling national data and information requirements. Current practice varies from countries individually monitoring and managing water quality, such as in the Amazon River basin, to attempts at full harmonisation of monitoring approaches driven by common legislation such as the Water Framework Directive in the Danube River basin. In the Mississippi River basin, for example, different agencies take responsibility for monitoring the main river and the sub-basins, leading to a lack of co-operation at the whole river basin scale. Long-term monitoring is an important basis for effective river basin management, and the co-operation achieved through the TNMN and the ICPDR in the Danube river basin is beginning to illustrate how results can be used to target management actions and show improvements in water quality downstream, including the delta and coastal areas. The EU strategy of selecting the best monitoring matrix is an important step towards better water quality management. In most situations, as in the Danube basin, basin-scale monitoring includes few, if any, indicators for newly emerging threats to water quality and this problem still needs to be addressed. All large-scale monitoring activities are resource intensive, hence statistical methods are being investigated to reduce costs by selecting fewer monitoring stations without loss of information. In addition, other indicators of water quality that have not traditionally been included in large scale monitoring programmes, such as faecal indicator organisms, might be useful to provide additional understanding of the influences on water quality.

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Appendix A1

Water quality assessment in many cases is a cross border activity; e.g. in the case of Hungary this is explicitly true, since 99% of its surface waters come from the bordering countries. To obtain representative results, the monitoring network should reflect the phenomena occurring in the water as close as possible. Sustaining and managing such systems is costly and time consuming, but their optimal functioning is vital from a scientific, environmental and economic aspect. In the view of these facts this example using CCDA shows the revision of the monitoring network of two rivers concerning Austria and Hungary, the Raab and the Danube (Figure A1/a). The specific aims of the example are:

- i) Examine the spatial monitoring networks of the rivers for redundancy,
- ii) Make a suggestion for optimizing the monitoring networks.

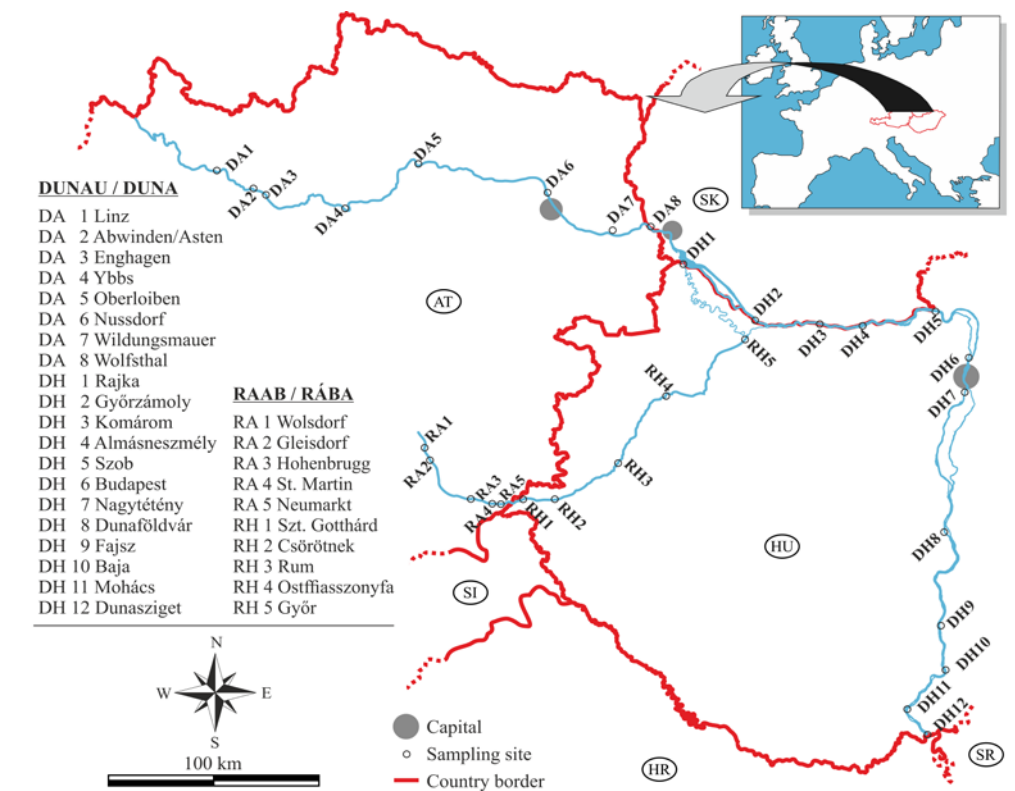


Figure A1. Locations of the areas shown as example on monitoring recalibration of rivers from the Danube Basin using CCDA

Combined cluster and discriminant analysis (CCDA) was used, first introduced by Kovács et al. (2014) to find not only similar, but homogeneous groups. During the search process a decision has to be made whether further division of some groups is necessary, or not. Cluster analysis is frequently used while searching for groups. However, if multiple groupings are possible (for example using hierarchical cluster analysis even N different classifications are possible, N denoting the number of different sample origins) one has to decide which classification to choose. While there are various methods for determining some kind of optimal classification (Davies and Bouldin, 1979; Dunn, 1973) in which members of the groups are similar; Combined Cluster and Discriminant Analysis (CCDA) (Kovács et al., 2014) goes one step further and aims to find homogeneous groups. It consists of three main steps: I) a basic grouping procedure, e.g. using hierarchical cluster analysis, to determine possible groupings; II) a core cycle where the correctness of the groupings from step I and the correctness of random classifications is determined using linear discriminant analysis; and a final evaluation step III, where a decision about iterative further investigation of sub-groups is taken.

Hence, the main idea of CCDA is that once the ratio of correctly classified cases for a grouping is higher than at least 95% of the ratios for the random classifications (i.e. the difference $d = \text{ratio} - q_{95}$ is positive), then at the level of $\alpha = 0.05$ the given classification is not homogeneous. Suggestions

for the necessary subdivision of groups (step III), a more detailed description of the method in general, as well as details about the R package “CCDA” used for the computations in this study can be found in Kovács et al. (2014).

The chosen joint Austrian-Hungarian section of the Danube Basin (Section 2) is highly affected by natural and anthropogenic phenomena. Numerous large tributaries and islands can be found in the selected sections of the Danube along with numerous water barrage systems including hydropower plants. One of the main tributaries is the Raab, with a watershed of 10,270 km² which is within the Danube basin. The full length of the Raab is 283 km, of which 72 km is in Austria and 211 km in Hungary. The mean runoff is 20-25 m³ s⁻¹. Like the Danube, the Raab is affected by external pressures mainly of anthropogenic origin. Numerous industrial facilities (such as leather, iron or food factories) and municipal sewage treatment plants can be found along the river.

In the case of both the Danube and the Raab the neighboring sampling sites were evaluated (1994-2004) using pH, oxygen demand [%], oxygen content, BOD₅, Ca, Mg, Na, K, Cl, SO₄, NH₄-N, NO₂-N, NO₃-N [mg l⁻¹], PO₄-P [μg l⁻¹] to find their homogeneous groups.

On the Danube, homogeneous sampling sites were only found in the Hungarian section (Fig. A2a). Heading downstream from the Austrian section the difference between the sampling sites continuously decreases. The magnitude of the change in the differences decreased to a much smaller degree in the Hungarian section than in Austria. At the end of the Hungarian section the last three sites formed a homogeneous group (DH10, DH11, DH12; Figure A1/b). Besides these three sampling sites examining the section between DA8 and DH1 would have been meaningless, because (i) it is highly affected by external inputs, (ii) the data of the sampling site in Slovakia is not accessible and (iii) the Gabčíkovo hydropower plant greatly changes the flow conditions and water quality in the area.

In the Raab, no homogeneous group of sampling sites were found. The changes in the difference between the sampling sites was much more diverse than for the Danube and frequently exceeded 20-30%. The continuous decrease downstream, as seen in the Danube, is not a characteristic of the processes in the Raab. Even the smallest differences did not reach the level of homogeneity (Figure A2B).

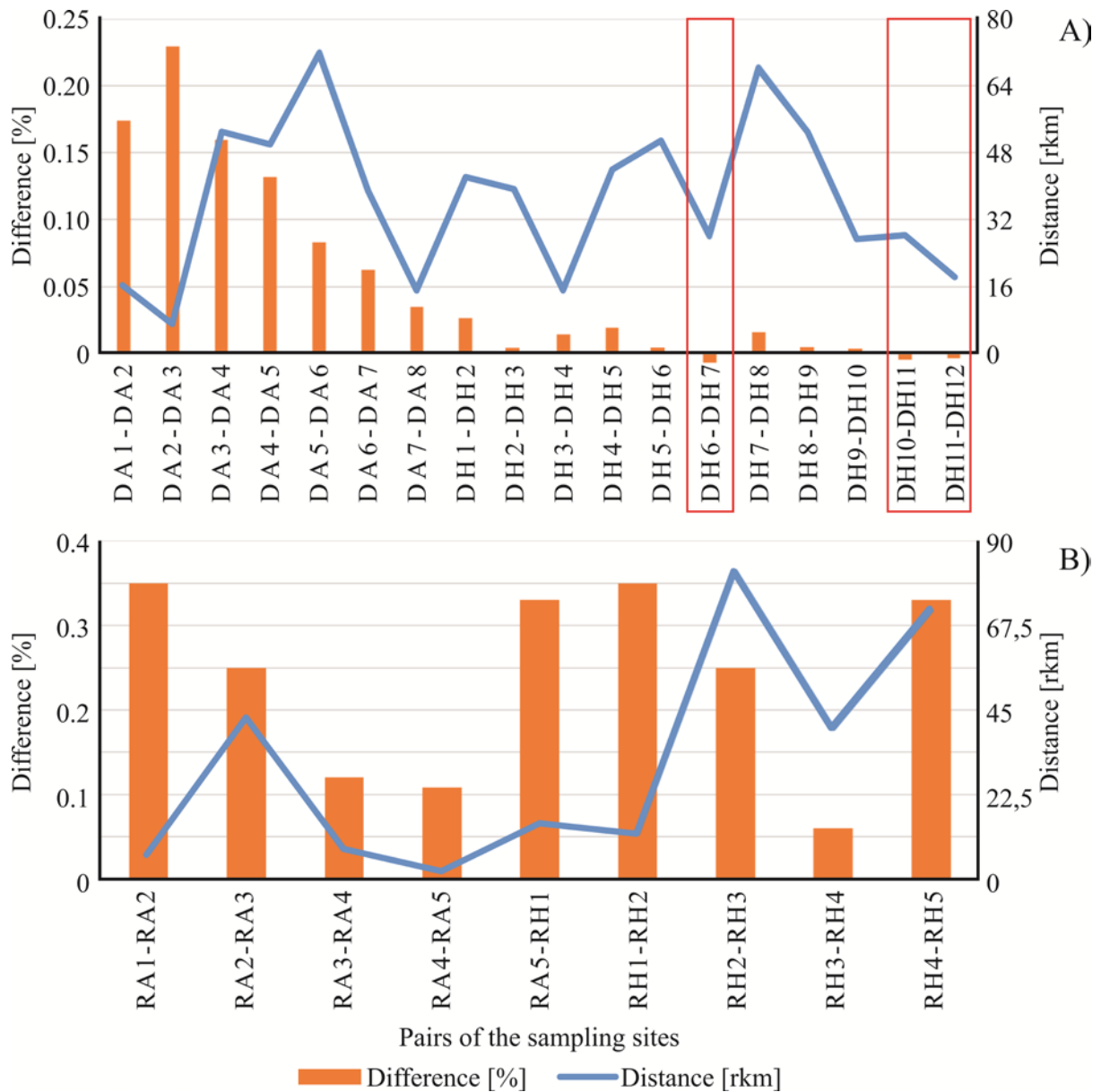


Figure A2. Pairwise comparison of sampling sites for the Danube A) and Raab B). Homogeneous sampling sites are marked with a red rectangle.

The examined sampling site pairs were in most cases inhomogeneous indicating differences in water quality. This cannot be simply explained by the distance between the sampling sites. In many cases, even sites close to each other (e.g. DA2-DA3, RA5-RH1 or RH1-RH2 in Figure A2 and A3) have large differences between them. Therefore, the explanation for the difference of the sampling sites is quite complex:

- i) As seen from the work of Sharp (1971), Sanders and Adrian (1978), and Sanders (1980) one of the most important separating factors are the tributaries, which can be taken into account as point

sources. Even in the case of sites close to each other a tributary can cause separation and result in different water quality. For example, DH3 and DH4 are close to each other but, the Vah entering the Danube splits them into two separate groups, as for RH1 and RH2 in the Raab separated by the Lafnitz (Figure A3b). In this context, it is important that samples should be taken below the confluence of a tributary where the two different water masses have fully mixed. The location of full mixing should be checked with profiles across the river in order to select the sampling site.

ii) Besides the tributaries, anthropogenic effects such as the ten water barrage systems in the Austrian section can cause separation between the sites. They change the morphology of the river bed along with flow conditions. This explains the large difference between sites DA2 – DA3, which are close to each other (without a tributary between them) but with the Abwinden-Asten hydro power plant.

iii) Again the heterogeneity of the sites in the Raab can be the result of anthropogenic activity (i.e. heavy industry on the course of the river (leather, iron or food factories). The outlets of the factories are thought to be responsible for the inhomogeneity of the sampling sites on the Raab, for both countries.

iv) As a last example the separating effect of larger islands should be considered (Szentendrei and Csepel islands). These also cause changes in water quality, and therefore heterogeneity of the sites, e.g. DH5-DH6 and DH7-DH8. Tabulated results and their further discussion can be found in Figures A3a and A3b.

would decrease the difference between the sites, especially at the source and between sites RA2-RA3, RH3-RH4 and RH4-RH5 ($d > 20\%$). The Raab, therefore, requires a denser monitoring network.

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